

**DETECTION OF TRACE LEVELS OF WATER**

**STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT**

This invention was made with Government support under Contract DEAC0676RL01830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

**BACKGROUND OF THE INVENTION**

Most machinery requires lubrication by oil to operate efficiently and reliably. Oil is also used as a hydraulic fluid in heavy equipment. Both lubrication and hydraulic oils can degrade by contamination from dirt, soot, process or wear materials, process chemicals, fuel dilution, or water. Water is the most common contaminant usually as a consequence of condensation, coolant leak or free water ingress during equipment cleaning or environmental exposure. Water at concentrations greater than about 1000 ppm can result in destructive wear and corrosion of parts as well as oxidation or degradation of the oil (Toms, L.A., *Machinery Oil Analysis: Methods, Automation & Benefits* 2nd ed. 1998, p. 141, Virginia Beach: Coastal Skills Training). Knowledge of the condition of oil in equipment is necessary in order to change the oil in a cost-effective manner. Premature oil change results in unnecessary cost as well as a waste in oil reserves. Changing the oil too late can result in part wear and possible equipment failure.

1 For early-warning and maintenance-scheduling purposes, detection limits of 10-50 ppm  
2 water in oil are desirable. Detection limits as low as 10 ppm are possible using Karl-Fischer  
3 titration. However, this technique is unsuitable for accurate, real-time, in-situ determinations of  
4 water levels in used oil because it requires a substantial sample size, is sample destructive and  
5 time consuming, and is subject to severe interferences from sulfur compounds present in most  
6 engine oils (ASTM D6304-00). Accurate, real-time, in-situ determinations of water can be made  
7 using Fourier-transform infrared (FTIR) spectroscopy, but the best currently achievable detection  
8 limits for water in oil are on the order of 250-500 ppm (Toms, L.A., *Machinery Oil Analysis:  
9 Methods, Automation & Benefits* 2nd ed. 1998, p. 141-144 Virginia Beach: Coastal Skills  
Training).

Photoacoustic spectroscopy ("PAS") has detection limits that are typically 10-1000 times  
lower than other purely absorption-based spectroscopies. A photoacoustic signal can be  
generated as follows. First, light stimulates a molecule within a sample. Such stimulation can  
include, for example, absorption of the light by the molecule to change an energy state of the  
molecule. Second, an excited-state structure of the stimulated molecule rearranges. During such  
rearrangement, heat, light, volume changes and other forms of energy can dissipate into an  
environment surrounding the molecule. Such forms of energy cause expansion or contraction of  
materials within the environment. As the materials expand, sound waves are generated.  
Accordingly, an acoustic detector mounted in acoustic communication with the environment can  
detect changes occurring as a result of the light stimulation of the absorbing molecule.

1 A method of estimating the volume fraction of water in kerosene or toluene using a 10.2  
2 cm diameter, 10-100 cm long cell by measuring the travel time of a ultrasonic wave through a  
3 temperature-controlled mixture and using a mathematical model has been reported (Tsouris, C. ,  
4 Tavlarides, L. *Volume Fraction Measurements of Water in Oil by an Ultrasonic Technique*. Ind.  
5 Eng. Chem. Res., 1993. **32**: p. 998-1002). Also, Hodgson reported a PAS sensor to detect oil  
6 in water (Hodgson, P., *et al.*, *Application of Pulsed Laser Photoacoustic Sensors in Monitoring*  
7 *Oil Contamination in Water*. Sensors and Actuators B, 1995. **29**: p. 339-344). These techniques  
8 do not have sufficient sensitivity to detect low levels of water in oil.

9  
10 Sensors based on PAS have recently been designed to monitor various other species  
11 including serum glucose levels (MacKenzie, H.A., *et al.*, *Advances in Photoacoustic Noninvasive*  
12 *Glucose Testing*. Clinical Chemistry, 1999. **45**: p. 1587-1595), hydrogen concentration ratios and  
13 CO<sub>2</sub> (Schlageter, B., *et al.*, *Development of an Optoacoustic Sensor Module for pH and/or CO<sub>2</sub>*  
14 *Determination in Aqueous Solutions*. Sens. Actuators, B, 1997. **B39**(1-3): p. 443-447), oil in  
15 water, hydrogen gas (Wan, J.K.S., M.S. Ioffe, and M.C. Depew, *A Novel Acoustic Sensing*  
16 *System for On-Line Hydrogen Measurements*. Sensors and Actuators B, 1996. **32**: p. 233-237),  
17 and biomass fermentation (Schmidt, K. and D. Beckmann, *Biomass Monitoring using the*  
18 *Photoacoustic Effect*. Sensors and Actuators B, 1998. **51**: p. 261-267). Lai and Vucic used PAS  
19 to monitor the degradation of motor oil by exciting the aromatic hydrocarbons at 355 nm (Lai,  
20 E.P.C. and R.S. Vucic, *Kinetic Study of the Degradation of Lubricating Motor Oil by Liquid*  
21 *Chromatography and Photoacoustic Spectrometry*. Fresenius J. Anal. Chem., 1993. **347**: p. 417-  
22 422). A method of detecting 3% water in ethanol by exciting a water/ethanol solution with 2GHz

1 microwave radiation and detecting the emitted acoustic signal with a PVDF microphone has been  
2 reported (Raikkonen, Oksanen, *Microwave Acoustic Sensing of Water in Hydrocarbon/Water*  
3 *Solutions*. Sensors and Actuators, 1994. A 45: p. 99-101). U.S. Patent 5,348,002 (Caro) issued  
4 September 20, 1994 disclosed a method of determining the amount of glucose or oxygen in  
5 biological fluids which have a high degree of scatter by generating an acoustic signal in the  
6 material, detecting the absorption coefficient of the material and using mathematical analysis  
7 techniques.

8  
9 The methods reported do not have sufficient sensitivity to detect low levels of water in oil  
10 and other absorbing substances in a nonwater sample. Therefore, there is a need for a technique  
11 to detect low levels of an absorbing substance in a nonwater system, such as water in oil. There  
12 is also a need for a rugged and sensitive technique that can be used in situ (in an on-line  
13 application).

#### 14 SUMMARY OF THE INVENTION

15 Provided is a method of determining the concentration of a substance of interest in a  
16 nonwater sample comprising: exciting the sample with a wavelength of light that is absorbed by  
17 the substance of interest; generating an acoustic wave within the sample; detecting the acoustic  
18 wave; and determining the amount of the substance of interest present in the sample. The  
19 substance of interest is preferably water. The sample is preferably oil. The substance of interest  
20 may be present in the sample at various concentrations, as described herein.  
21  
22

1 Also provided is a preferred method of determining the concentration of water in an oil  
2 sample which contains less than 1% water comprising: exciting the sample with light having a  
3 wavelength water absorbs; generating an acoustic wave within the sample; detecting the acoustic  
4 wave with a transducer in acoustic communication with the sample; and determining the amount  
5 of water present in the sample by processing the signal detected by the transducer. In this  
6 preferred embodiment, it is preferred that the light has a wavelength less than 1 mm.  
7

8 Also provided is an apparatus for detecting the concentration of a substance of interest in  
9 a nonwater sample comprising an excitation source which provides light having a wavelength  
10 that is absorbed by the substance of interest; a sample in light contact with the source; and a  
11 detector in acoustic communication with the sample. Preferably, the apparatus is used to detect  
12 the concentration of water in oil. The apparatus is also useful to detect the presence of water in  
13 nonwater chemicals, among other substances.  
14

15 A preferred use of the apparatus is to determine the concentration of water in an oil  
16 sample where the apparatus comprises: an excitation source which provides pulsed or modulated  
17 light having a wavelength water absorbs; a prism cell in light contact with the excitation source;  
18 and a transducer in acoustic communication with the sample.  
19

## 20 BRIEF DESCRIPTION OF THE DRAWINGS

21 Figure 1. PAS calibration curves for clean hydraulic (+), transmission (•), and engine (x) oils  
22 with water. The error bars represent  $\pm 3$  standard deviations.

1  
2 Figure 2. PAS signal for transmission oil with standard additions of water. The error bars  
3 represent  $\pm 3$  standard deviations.  
4

5 Figure 3. PAS response for NIST SRM 8705 and this oil 'dried' with molecular sieve for 48  
6 hours. The error bars represent  $\pm 1$  standard deviation.  
7

## 8 DETAILED DESCRIPTION OF THE INVENTION

9 Although the description herein is directed to preferred embodiments, it should be  
10 understood that the invention is not limited to the specific embodiments described. The methods  
11 described herein provide nondestructive sampling, high sensitivity, and nearly instantaneous data  
12 collection capabilities. No moving parts are required, and rugged solid-state light sources,  
13 sampling cells and detectors can be used. The methods and apparatuses described herein are  
14 selective for species of interest. The methods and apparatuses described herein can be used in a  
15 stand-alone application, either as a bench-top apparatus or a portable apparatus, can be used in an  
16 in-line flow stream application, or used for remote sensing applications.  
17

18 Samples which may be analyzed include oil, hydrocarbon-based fuels, packaged foods,  
19 chemicals, and other samples which contain an absorbing substance that is desired to be either  
20 detected or quantitated, and where the absorbance spectra of the substance of interest and the  
21 sample are different. In a preferred embodiment, the sample is oil. One class of samples is  
22 biological fluids.

1  
2 The substance of interest which is detected or quantitated may be any absorbing  
3 substance. An "absorbing substance" is one which absorbs at least some of the light which is  
4 applied. Absorbance indicates the absorbing substance has an absorbance that is detectable above  
5 the background absorbance of the sample. Absorbing substances include water (light water,  
6 heavy water), trace chemicals, compounds comprising OH groups (e.g., alcohols), solvents, and  
7 additives such as those present in oil and hydrocarbon-based fuels. The sample may contain  
8 immiscible substances, such as a large amount of water in an oil sample.

9  
10 Nonwater samples are those containing less than 100% water. Particular classes of  
11 samples include those with less than 80% water, less than 60% water, less than 50% water, less  
12 than 40% water, less than 20% water, less than 10% water, less than 1% water, less than 1000  
13 ppm water, less than 250 ppm water, less than 50 ppm water and all intermediate ranges therein.  
14 Nonwater samples include oil.

15  
16 Determining the amount of the substance of interest in the sample may be performed by  
17 any method known in the art, those methods described herein, and by modifications of the  
18 methods known in the art and described herein that may be performed by one of ordinary skill in  
19 the art without undue experimentation. One such method is the method of standard additions.  
20 The presence of the substance of interest in the sample may also be detected using the methods  
21 and apparatuses described herein.

1 The excitation source may be any source that generates a wavelength of light that is  
2 absorbed by the substance of interest. The light may have any wavelength or combination of  
3 wavelengths that is sufficient to cause a detectable signal. The light is preferably pulsed or  
4 modulated. The light may come from a pulsed source, or a chopper may be used to modulate  
5 light which is continuous. In addition, one pulse of light from a source may be used to generate a  
6 signal.

7  
8 Various light sources are useful in the methods described herein. These include, but are  
9 not limited to lasers (including solid-state Er-YAG, quantum-cascade solid-state lasers, Pb-salt  
10 diode lasers, and other infrared diode lasers) and flashlamps, including Xe flashlamps used in  
11 trigger sockets, for example (wavelengths can be selected with notch filters, among other  
12 methods known in the art). The selection of the light source used is made by considering the  
13 absorbance spectrum of the substance of interest and the particular transitions desired to be  
14 excited, as is well known in the art. It is preferred that the light be provided by a source of  
15 electromagnetic radiation having a wavelength including but not limited to x-ray, ultraviolet,  
16 visible, near infrared, infrared, and combinations thereof. One class of wavelengths is the  
17 microwave range. Another class of wavelengths has wavelengths shorter than microwave. For  
18 example, to detect water, light in the IR range (770 nm-50  $\mu\text{m}$ ), is useful because water absorbs  
19 light of that range. A broadband source may be used with appropriate filtering devices to select  
20 the wavelength of interest. A multiwavelength source may be used with dielectric mirrors or  
21 filters to detect more than one wavelength simultaneously. Any light source may be used that is  
22 absorbed by the substance of interest and provides sufficient energy to generate an acoustic wave



1 that is detectable above background. The detectability of an acoustic wave is affected by the  
2 detector characteristics and data collection apparatus used, as is known in the art. Laser diodes  
3 provide sufficient monochromatic light to generate a detectable acoustic wave and are  
4 particularly useful in miniaturized versions of the methods and apparatuses described herein.  
5 Use of a Xe flash lamp and notch filter can also provide appropriate light at a significantly lower  
6 cost.

7  
8 One embodiment of the invention provides pulsed or modulated monochromatic light to a  
9 sample at a wavelength where water absorbs strongly and other components of the sample do not.  
10 In petroleum-based oils, hydrocarbon-based fuels (e.g. gasoline, diesel, kerosene), and most  
11 organic solvents, one such wavelength is about  $2.94\ \mu\text{m}$  where pure water has its highest  
12 absorptivity ( $1.2 \times 10^4\ \text{cm}^{-1}$ ) due to O-H stretching vibrations. For synthetic oils having  
13 polyolester or phosphate ester base stocks, this wavelength is somewhat shorter (about  $2.75\ \mu\text{m}$ ).  
14 Other wavelengths are useful, depending on the sample matrix. These wavelengths are easily  
15 determined by one of ordinary skill in the art without undue experimentation using the methods  
16 described herein and methods known in the art. Another embodiment of the invention uses light  
17 which is not monochromatic. Wavelength selection may be made with appropriate filters, for  
18 example.

19  
20 Various sampling devices can be used in the method described herein. It is preferred that  
21 there is a transparent surface such as a window or prism to transmit light into the sample, but it is  
22 not required. The invention does not require sample cells that are on the order of 10 cm diameter

1 and 10-100 cm long. One preferred sample device is a layered prism cell, as described in U.S.  
2 Patent Application No. 09/105,781, filed June 1998, and Autrey, T., *et al.*, *A New Angle into*  
3 *Time-Resolved Photoacoustic Spectroscopy: A Layered Prism Cell Increases Experimental*  
4 *Flexibility*. Rev. Sci. Instrum., 1998, **69**(6): p. 2246-2258, both of which are hereby incorporated  
5 herein by reference to the extent not inconsistent with the disclosure herein. The layered prism  
6 cell includes a first block of material with opposing front and back surfaces. The front surface  
7 comprises a substantially planar portion configured to be against a sample. The back surface  
8 comprises a substantially planar portion configured to be joined to a transducer. The back  
9 surface is substantially parallel to the front surface. The first block of material also has a pair of  
10 opposing side surfaces joined to opposite ends of the front and back surfaces. The opposing side  
11 surfaces are a first opposing side surface and a second opposing side surface. The first opposing  
12 side surface is configured for passage of light therethrough and extends at a first oblique angle  
13 relative to a plane containing the substantially planar portion of the front surface. The second  
14 opposing side surface extends at a second oblique angle relative to the plane containing the  
15 substantially planar portion of the front surface. There may also be a second block separated  
16 from the first block by a shim. The second block may be from the same material or a different  
17 material than the first block. The sample cell also has embodiments in which a sample reservoir  
18 or similar structure is against a surface of a block, regardless of whether a second block is  
19 provided.

20  
21 Both transmission and internal-reflectance geometries can be used in flow-through cell  
22 configurations, as well as static sampling. These cells and methods of using the cells are known

1 in the art. It is recognized that light can be either refracted or reflected by a material, depending  
2 on an angle with which the light impacts a surface of the material. A critical angle is determined  
3 by the relative refractive indices of materials joining at a surface. Specifically, if light passes  
4 from a first material having a larger refractive index to a second material with a lesser refractive  
5 index, a critical angle can be defined relative to an axis normal to a surface where the two  
6 materials meet. If light impacts the surface where the two materials meet at an angle greater than  
7 the critical angle, the light will predominantly reflect from this surface. If light impacts the  
8 surface where the two materials meet at an angle less than the critical angle, the light will  
9 predominantly pass into the cell material and refract within the cell material. A critical angle can  
10 be calculated from application of Snell's law, as known in the art, and the relative amount of  
11 refraction and reflection can be determined.

12 Incident light may be directed into the cell at an appropriate angle such that the light  
13 reflects from surfaces of the material to be contained internally in the cell material. Such  
14 reflections are referred to as internal reflections. It is known that some of the light will actually  
15 extend slightly outward of a surface of the material as the light reflects internally from the  
16 surface. Although the light extends slightly outward of the surfaces of the material as it is  
17 reflected within the material, the light continues along the general path illustrated by the light  
18 beam. Accordingly, if cell material is provided adjacent to a sample, a light beam can be  
19 provided to be internally reflective within the cell material and yet to stimulate molecules within  
20 the sample. Such use of internal reflections for stimulating molecules within a sample can be  
21 advantageous in situations where a sample is generally not transparent to a light source, such as,  
22

1 for example, when the sample is relatively turbid or optically dense. The amount by which the  
2 light waves penetrate into a sample can be adjusted by changing a wavelength of the light, or by  
3 changing an angle at which the light internally reflects from surfaces of the cell material.  
4

5 Various detection and data processing methods may be used in the methods of the  
6 invention as are known in the art. For example, a digital oscilloscope can be used to digitize the  
7 signal from the detector. Digitizing electronics can be triggered by the incident light pulse, or  
8 other embodiments known to the art. Data acquisition cards can also be used. Detectors are  
9 preferably acoustic microphones or transducers that are in acoustic communication with the  
10 sample. A detector in acoustic communication with the sample, as used herein, is defined as a  
11 detector that is acoustically coupled with the sample so that the detector receives useful  
12 information from the sample by acoustic transmission. Such coupling may be accomplished by  
13 having the detector in direct contact with the sample or by using a gas, liquid, solid, or  
14 combinations thereof therebetween to acoustically couple the detector with the sample. One  
15 embodiment of the invention uses one or more than one detector in acoustic communication with  
16 the sample. Transducers with different resonant frequencies can be used to improve selectively,  
17 as described in U.S. Patent Application No. 09/322,910, filed June 1, 1999, incorporated by  
18 reference herein to the extent not inconsistent with the disclosure herewith. Photoacoustic  
19 selectivity using different resonant frequencies is achieved by analyzing the response of the  
20 various frequency transducers to the time-dependent release of heat from the electronic and/or  
21 vibrational excited state species. For example, the response of a 1MHz transducer and a 5MHz  
22 transducer will have a characteristic shape defined by the concentration and excited state lifetime

1 of the species absorbing the energy. The time-dependent response provided by an ultrasonic  
2 transducer from the competitive absorption of light by multiple species may be mathematically  
3 described and analyzed for the unique solution that provides the concentration of each of the  
4 species, as described in further detail in U.S. Patent Application No. 09/322,910.

5  
6 An electrical interconnect may extend from the detector to electrically couple the detector  
7 with circuitry for either processing or displaying signals generated by the detector.

8  
9 Optics for directing the light into the sample cell are known in the art and may include  
10 wedges, filters, beam splitters, irises, fiber optics, lenses, as well as other optical devices.

11  
12 "Oil" is a naturally-occurring or synthetic substance or mixture of substances that contains  
13 hydrocarbons, and may optionally contain other substances such as additives (including  
14 antioxidants, detergent-dispersants, wear preventives, rust preventives, sequestering agents,  
15 friction-coefficient modifiers, defoaming agents, colorants, seal-swelling agents and  
16 viscosity-index improvers) and heteroatom-containing substances such as alcohols and other  
17 oxygen-, sulfur- or nitrogen-containing compounds. "Oil" includes all petroleum-based, natural,  
18 and synthetic oils, including all types of engine oils, such as transmission and hydraulic, all  
19 edible oils, including olive oil, vegetable oil and canola oil, and other oils.

20  
21 The methods described herein can be used for on-line analysis of lubricating oils in large  
22 or critical-mission machinery such as stationary diesel and gas-turbine engines for power

1 generation and marine propulsion, locomotive engines, heavy equipment, military weapons  
2 platforms, trucks and automobiles. Also, hydraulic fluids in heavy equipment and aircraft can be  
3 analyzed. The methods described herein can also be used for process monitoring in food  
4 production and organic chemical production/use (for example, production of polymers), as well  
5 as-humidity sensors. Other applications will be apparent to one of ordinary skill in the art.  
6

7 Using the methods and devices described herein, trace levels of water in nonwater  
8 samples, including petroleum and synthetic lubrication oils can be detected. Trace levels of  
9 water in petroleum oils using PAS can be performed at detection levels at least 5-10 times below  
10 those obtained by conventional absorption-spectroscopic techniques. Samples with water  
11 concentrations of less than about 1000 ppm, less than about 750 ppm, less than about 500 ppm,  
12 less than about 250 ppm, less than about 100 ppm, less than about 50 ppm, and lower, and all  
13 intermediate ranges therein can be detected in an oil sample using the methods and apparatuses  
14 described herein. Detection limits of 50 ppm are easily obtainable, and limits of 10-20 ppm are  
15 achievable with optimization of the methods and apparatuses described herein. Detection limits  
16 from ultratrace up to nearly 100% of the substance of interest in a nonwater sample are provided,  
17 along with all intermediate ranges therein.  
18

19 An appropriate wavelength for use in sample excitation can be selected by methods  
20 known in the art, or methods described herein. One method of selecting an appropriate  
21 wavelength for excitation is described here. The absorbance spectrum of water or the substance  
22 of interest is measured along with the absorbance spectrum of the major components of the

1 sample. Those spectra are compared, and a wavelength where the substance of interest absorbs  
2 more strongly than the components of the sample is selected. As long as the substance of interest  
3 absorbs the wavelength selected, the measurements may be performed using appropriate  
4 mathematical manipulation of the data, as known in the art.

5  
6 The techniques described herein are useful in determining the concentration or presence  
7 of water in oil in a static sample or may be used in a flowing stream. One embodiment of using  
8 the invention in a flowing-stream environment comprises positioning a light source and a  
9 detector on opposite sides of a sample contained in, for example, a tube such as a pipe. In this  
10 embodiment, the light source will excite the substance of interest. The acoustic wave generated  
11 will travel to the detector. The contribution of the distance between the light source and the  
12 detector to the signal can be taken into account by mathematical relationships known to those in  
13 the art or readily determinable without undue experimentation. Another embodiment has the  
14 detector on any side of the light source. The detector may also be some distance from the light  
15 source and on the same side, provided that acoustic coupling between the sample and detector is  
16 maintained. Other geometries and arrangements between components of the apparatus are  
17 useful, as known in the art.

#### 18 19 Examples

20 Unused transmission, hydraulic, and engine-oil samples from the U.S. Army tank  
21 maintenance facility at the Yakima Firing Range, WA were studied. The transmission and  
22 hydraulic oils were petroleum oils. The transmission fluid was a Dextron-type petroleum-based

1 fluid. The hydraulic fluid also was largely petroleum-based and conformed to MIL H 83232.  
2 The engine oil was a synthetic polyolester based oil for use in gas turbine engines (MIL L 23699)  
3 and contained few, if any, additives. The transmission and engine oils are the types currently  
4 used to lubricate M1 Abrams tanks. A reference mineral oil from the National Institute of  
5 Standards and Technology (SRM 8507) certified to have 76.8 ( $\pm$  2.3) ppm water was also tested.  
6 The method of standard additions was used to prepare samples of clean oil with known relative  
7 water contents. Briefly, 10-20 mL of oil was placed in a tared 22-mL glass vial with a stir bar.  
8 While on the balance, aliquots of water (ca. 5-10  $\mu$ L) were added. The actual amounts added  
9 were determined by weight. After capping the vials, the oil/water mixtures were then stirred for  
10 15-30 minutes or until complete miscibility was obtained as determined by visual inspection.  
11 Samples of the clean oils and the reference material were also treated for at least 15 hours with a  
12 molecular sieve (5 g 4Å pore size 4-8 mesh beads, which had been heated 1 week at 120°C in 10  
13 mL oil) to remove water that might have already been present in the oils.

14  
15 Data was collected using the flow-through layered prism cell (described in Autrey, T., *et*  
16 *al.*, *A New Angle into Time-Resolved Photoacoustic Spectroscopy: A Layered Prism Cell*  
17 *Increases Experimental Flexibility*. Rev. Sci. Instrum., 1998, **69**(6): p. 2246-2258) with a  
18 sapphire entrance prism, quartz exit prism, and an optical pathlength of 0.76 mm. Acoustic  
19 communication with the transducer (0.25-inch diameter, 5-MHz Panametrics) was facilitated by  
20 an ultrasonic couplant fluid (Sonic Instruments). Excitation light of 2.93  $\mu$ m (3416 cm<sup>-1</sup>) light  
21 was generated by Raman shifting (900 psi deuterium in a 1-m Raman cell [LightAge,  
22 #101PAL.RC-1.0]) 1.064-nm light from a pulsed Nd-YAG laser (Continuum, #NY61-20)



1 operating at 20 Hz. Filters and mirrors were used to filter out the unwanted Raman lines. Energy  
2 per pulse was about 20  $\mu$ J. The signals from the transducer were amplified using a preamplifier  
3 (Panametrics, model 5670, 40dB) and waveforms collected on a digital oscilloscope (Lecroy,  
4 model 9362). The water signal was monitored using a computer interface and a boxcar averager  
5 (Stanford Research Systems). Data collection software queried the boxcar averager and  
6 integrated the signal. All waveforms were signal averaged over 500 shots. The photoacoustic  
7 signal was determined by integrating the signal voltage over the time period selected by the  
8 boxcar. Data reported are the averages of twenty 500-pulse signal-averaged events (i.e., 500 s  
9 total analysis time). Detection limits were calculated ( $S/N=3$ ) based on the standard deviation of  
10 the signal of the blank ( $n=20$ ).

11 To demonstrate the selectivity of the approach, water and a series of four neat organic  
12 solvents that did or did not contain hydroxyl functional groups were tested. For the solvents that  
13 contained the hydroxyl functional groups (water, methanol and decanol), strong absorption at  
14 2.93  $\mu$ m due to O-H stretching vibrations was expected. Little absorption was expected for the  
15 other solvents that lacked the hydroxyl functional group (methylene chloride and carbon  
16 tetrachloride). The PAS results obtained for these five solvents were:  
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Solvent	Peak-to-Peak signal (mV)
methylene chloride	$1.8 \pm 0.5$
carbon tetrachloride	$5.7 \pm 1$
water	$47 \pm 1$
methanol	$228 \pm 2$
decanol	$230 \pm 2$

These results show the clear selectivity of the PAS technique for substances that contain hydroxyl groups when a  $2.93 \mu\text{m}$  excitation wavelength is used. The four-fold higher sensitivity to methanol and decanol than to water stems from the more favorable acoustic transmission properties of the alcohols. The very low signal levels observed for the nonhydroxylated solvents may actually reflect the presence of trace levels of water in these nominally neat solvents.

The absorption maximum of pure water ( $A=12,262 \text{ cm}^{-1}$ ,  $\epsilon=221 \text{ M}^{-1} \text{ cm}^{-1}$ ) is at  $2.935 \mu\text{m}$  ( $3407 \text{ cm}^{-1}$ ) and the wavelength region where 95% of the maximum absorbance occurs extends from about  $2.90\text{-}2.97 \mu\text{m}$  (Hale, G.H. and M.R. Querry, *Optical constants of water in the 200 nm to 200  $\mu\text{m}$  wavelength region*. Appl. Opt., 1973. 12: p. 555-563; Wieliczka, D.M., S. Weng, and M. R. Querry, *Wedge shaped cell for highly absorbent liquids: infrared optical constants of water*. Appl. Opt., 1989. 28: p. 1714-1719). Although the value of the absorption coefficient for water in a petroleum-based oil matrix was unknown, it is not likely to change significantly, therefore, this wavelength region was selected as the most likely to yield the low detection limits required. Standard curves for clean hydraulic, transmission, and engine oils with water using  $2.93 \mu\text{m}$  as the excitational wavelength are plotted in Figure 1. Detection limits for water were

1 calculated to be 60 ppm in hydraulic oil, 45 ppm in transmission oil and 515 ppm in engine oil.  
2 The detection limits for the hydraulic and transmission oils are 5-10x lower than those obtainable  
3 with FTIR.  
4

5 According to Toms (Toms, L.A., *Machinery Oil Analysis: Methods, Automation &*  
6 *Benefits*. 2nd ed. 1998, p. 143, Virginia Beach: Coastal Skills Training) the absorption maximum  
7 for water in synthetic oils splits into two bands at 2.75 and 2.82  $\mu\text{m}$  (3640 and 3550  $\text{cm}^{-1}$ ). Light  
8 absorption by the synthetic oil at 2.93  $\mu\text{m}$  was due mainly to antioxidant additives, although  
9 some absorption due to water was present and yielded the observed PA response. The location of  
the water absorption bands by differential FTIR analysis of the engine oil as received and after  
addition of 1000 ppm water was confirmed (data not shown). Consequently, at the excitation  
wavelength used, one would not be expected to be able to detect water in this engine oil by PAS  
with the same sensitivity achieved for the hydraulic and transmission oils.

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15 In a second experiment, the transmission oil and a wider range of water contents was  
studied, including a sample of the oil treated with a molecular sieve to remove water initially  
16 present. The results showed a linear response to about 1800 ppm added water (Figure 2). Above  
17 this value incomplete miscibility occurred (emulsification was not attempted) and so a lower  
18 signal was obtained than expected. To determine the amount of water present in the original oil,  
19 the molecular-sieve material was added to this oil to remove all water and the PA signal was  
20 measured. The signal obtained corresponded to an "added water" concentration of ~170 ppm,  
21 suggesting that the original concentration of water in the oil was 170 ppm.  
22

1  
2 In a third experiment, two samples of the NIST reference oil, one as received and one  
3 after treatment with the molecular sieve for 48 hours to remove water, were analyzed. The  
4 results of these analyses (Figure 3) clearly show the ability of PAS to distinguish between 77 and  
5 0 ppm water in this sample (the error bars in the figure are one standard deviation of the data).  
6 The calculated detection limit for this sample was 62 ppm water. This is shown as a dashed line  
7 in Figure 3.

8  
9 Although the description above contains many specificities, these should not be construed  
as limiting the scope of the invention but as merely providing illustrations of some of the  
presently-preferred embodiments of this invention. For example, light sources and sample cells  
different from those specifically illustrated herein may be used. Also, different detection and  
data analysis and collection devices may be used from those specifically illustrated herein. Thus,  
the scope of the invention should be determined by the appended claims and their legal  
equivalents, rather than by the examples given. All references cited herein are hereby  
incorporated by reference to the extent not inconsistent with the disclosure herewith.